PHYTOTOXICOLOGY SOIL AND VEGETATION ASSESSMENT SURVEYS: ICI LIMITED, COURTRIGHT 1991 AND 1992

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Report prepared by:

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1.0 INTRODUCTION

The Phytotoxicology Section of the Air Resources Branch has conducted vegetation assessments in the western portion of Lambton County since the early 1970s. A network of permanent sample collection sites was established, at that time, to investigate the three principal sources in the area; ICI/CIL Lambton Works, Ontario Hydro's Lambton Generating Station, and Detroit Edison's St. Clair Generating Station. The ICI/CIL (Lambton Works) superphosphate plant has been a substantial source of hydrogen fluoride (HF) resulting from the production of superphosphate fertilizer, fugitive emissions from open gypsum wastes, and from evaporation of process water from the settling ponds. As a consequence, vegetation injury caused by fluoride in the area has been documented by Phytotoxicology field investigators since 1969. Concerns regarding the HF emissions were initially raised because of obvious damage to vegetation, and because of the potential health impacts on livestock that ingest fluoride contaminated forage.

CIL initiated a decommissioning plan to cap the gypsum waste material on the property (a stack over 15 meters in height and covering approximately 40 hectares) with several feet of clay, topsoil and vegetation. This project was complete in late summer, 1989, and an additional 0.5 meter of cover was added to the top of the gypsum waste site in the summer of 1992. As a result of these actions, fluoride emissions from the gypsum waste were expected to be eliminated.

ICI purchased CIL in 1990. ICI is continuing development work to further treat and reuse water within the settling ponds. There are an estimated 700 million gallons of liquid contained within the settling ponds. ICI has lime-treated approximately 660 million gallons to reduce the phosphate and fluoride concentrations in the ponds, and are continuing to treat collected leachate from the gypsum waste site on an as-needed basis.

The original vegetation sampling network established in the vicinity of ICI/CIL consisted of nine (9) silver maple foliage sites at which visible observations of foliar damage were made and at which foliar, and occasionally, soil samples were collected. A network of ten (10) forage (grass) sampling sites were also established in the vicinity of ICI/CIL, in 1980.

This report summarizes the findings of visual vegetation damage assessments and maple foliage and grass chemistry at sampling sites in 1991 and 1992. The results of chemical analysis of soils collected at the maple foliage collection sites in 1991 are also summarized.

2.0 METHODOLOGY

The vegetation assessment surveys in the vicinity of ICI were conducted by J. Craig Kinch in late August, 1991 and by R. Jones in late August 1992. The surveys were conducted in a similar manner to those surveys in the preceding years, with some notable exceptions.

At each of the nine sites shown in Figure 1, silver maple was examined for HF injury. Duplicate foliar samples were collected from all nine established sites in 1991 and analyzed for fluoride in both washed and non-washed samples, as in previous years. Samples were also analyzed in 1991 for sulphur and uranium. In 1992, duplicate samples were collected only from Sites 1, 6, 7, 8 and 11 and submitted for fluoride analysis on a non-washed basis.

In 1991 and 1992, as in previous years, intensive grass sampling programs were conducted in close proximity to the ICI facility (Figure 2). Duplicate grass samples were collected in August of each of the two survey years at each of the ten (10) sampling sites. Samples collected in 1991 were submitted for fluoride, sulphur and uranium analysis. Samples collected, in 1992, were submitted only for fluoride analysis, as in previous years.

Unlike previous years, soil samples were collected from each of the silver maple collection sites in 1991. Duplicate soil samples (0-5 cm) were collected from a 100 m^2 area at each site. Each sample consisted of a minimum of 50 individual cores collected from random locations within the sample area. Samples were collected using a stainless steel corer. Processed soils were analyzed for fluoride, and ^{238}U, ^{235}U, ^{40}K and ^{226}Ra radioisotopes.

All vegetation samples were collected into clean plastic bags and transported to the Phytotoxicology processing lab. One-half of each sample was washed for 30 seconds in an aqueous detergent solution (0.05% Alconox and 0.05% EDTA in distilled water), followed by three 10-second rinses in distilled water. The samples were oven-dried, ground in a Wiley-mill and stored in glass bottles. Soil samples were split into two sub-samples with both being air-dried, pulverized to pass through a 60 mesh sieve and stored in glass bottles. Processed vegetation and one of the soil sub-samples were forwarded to the Ministry of the Environment laboratory in Etobicoke for the chemical analyses described above. The second unprocessed sub-sample of soil was subsequently submitted to the Ministry of Labour laboratory in Etobicoke for radioisotope analysis.

3.0 RESULTS AND DISCUSSION

Injury Observations

In 1991, as in all previous years in which the survey was conducted, injury was observed on silver maple foliage. Injury was observed at Sites 1, 3, 7, 8 and 13. In all cases, the injury was considered to have been trace to light and involved terminal necrosis, and in some cases chlorosis and insect gall formation. However, unlike other years, the injury was not specific to sites located close to the facility and did not appear to be the result of fluoride, but rather the result of insects, disease and/or climate. Less injury was observed in 1992 and the damage was similarly related to natural factors and not suspected to be the result of HF emissions from the plant.

Silver Maple Foliar Chemistry

The results of analysis of non-washed and washed silver maple foliage are presented in Table 1. The fluoride concentration in non-washed maple foliage consistently exceeded the Phytotoxicology Upper Limit of Normal (ULN) guideline (see Appendix) for foliage collected in rural areas at the three sites closest to the facility (Sites 1, 6 and 11) each year until 1989. Similarly, foliar fluoride concentrations were elevated in foliage collected from Sites 2, 7 and 12, located approximately 3 km from the facility, during the period from 1983 to 1987. There were, however, no exceedences of the rural ULN for fluoride in silver maple foliage at any of the sites, in 1991 or 1992. There was still a tendency in 1991 for sites close to the facility to have elevated fluoride concentrations relative to more distant sites. However, this pattern was virtually non-existent in 1992, with the possible exception of slightly-elevated fluoride concentrations at Site 1. These data, therefore, suggest that the trend towards reduced fluoride emissions, which was evident in 1989, was accelerated through 1991 and 1992 to the point that the majority of sites had fluoride concentrations in 1992 that were at or near background concentrations.

Chemical concentrations in washed foliage are often compared to non-washed foliar concentrations to examine the fraction of contaminant that has been deposited on foliar surfaces in particulate form. The analytical results for fluoride concentrations in washed foliage are also presented in Table 1. It is evident from this data that very little surfical fluoride contamination was present in any year. Results for 1991 would indicate that the differences between washed and non-washed foliage represent sampling and laboratory variability rather than the presence of fluoride-containing particulate.

Sulphur and uranium concentrations in washed and non-washed silver maple foliage collected in 1991 are presented in Table 2. In no case did sulphur concentrations in non-washed foliage exceed the rural ULN guideline. However, slightly elevated concentrations of sulphur in foliage collected at Site 1 compared with other sites did indicate that the facility may be a marginal sulphur source. Differences between washed and non-washed foliar sulphur concentrations were minimal and probably within the range explainable by sampling and analytical error. Uranium concentrations were below the detection limit in both washed and non-washed foliage at all of the sample sites.

Grass Foliar Chemistry

Fluoride concentrations in grass are summarized in Table 3 along with the various benchmark values used to evaluate the significance of fluoride concentrations in forage. There is a general trend in the data toward reducing fluoride concentration in forage in the vicinity of the facility from 1987 to 1992. In 1987, all but one of the forage sites (Site 10) exceeded the rural ULN. In 1991 and 1992, only one site exceeded the rural ULN (Site 8 - 200 m SSE). While fluoride concentrations in forage were not historically the highest at Site 8, this was the site that most consistently exceeded the rural ULN for forage in the past. Although forage at Site 8 still exceeded the ULN in 1992 (13.5 ug/g), there has been consistent decreases in foliar fluoride concentrations at this site from 1984 through 1992.

Sulphur concentrations in forage in the vicinity of ICI were below the rural ULN and did not demonstrate any consistent pattern with distance from the facility (Table 4). Similarly, uranium concentrations in forage were all below the detection limit.

Soil Chemistry

Fluoride concentrations in surface soil collected in 1991 are summarized in Table 5. With the exception of Site 6, the sites closest to the facility (Sites 1 and 11) had substantially higher concentrations of fluoride in soil than more distant sites. The mean concentration of fluoride in soils collected from Sites 1 and 11 was 175 ug/g compared to the mean concentration for sites 2.6 km or more from the facility of 61 ug/g. However, soil fluoride concentrations can be highly variable and greatly influenced by soil clay concentrations. Although no ULN has been established for fluoride in soils, the average world-wide fluoride content of soils has been calculated to be 320 ug/g, with the range for most soils being 100 to 400 ug/g. In addition, while fluoride compounds emitted from industrial sources may be readily soluble in soils, much of the ion may be fixed by soil components including clays, calcium and phosphorus and therefore is not available to plants. Fluoride uptake by plants from temperate zones is generally thought to be passive with many plants actively excluding

fluoride from root uptake. Therefore, the availability of fluoride to plants may not be closely related to total or soluble fluoride in soil. In this study there was no consistent relationship between soil fluoride and concentration of fluoride in silver maple foliage. Soils were not collected in the previous studies or in the 1992 survey.

Radioisotope concentrations in surface soils collected in the vicinity of the ICI facility are also summarized in Table 5. There was no source-related trend evident for any of these isotopes in surface soil.

4.0 SUMMARY

Vegetation assessment surveys were carried out in the vicinity of the ICI Lambton works in 1991 and 1992. The survey design was similar to that conducted in each of the sixteen previous years with the following exceptions; 1) soils were collected at each of the silver maple sampling locations in 1991, 2) soil and vegetation samples collected in 1991 were submitted for sulphur and uranium in addition to fluoride, 3) soils were analyzed for radioisotope concentrations, and 4) the 1992 survey was conducted for vegetation only and involved a reduced number of silver maple sampling sites.

Although some injury was seen on silver maple in the 1991 and 1992 surveys, the injury was not specific to sites in the historical zone of influence of the facility. The injury was thought to be due to natural factors rather than the result of HF emissions from the plant.

With few exceptions, fluoride concentrations in silver maple foliage and grass were the lowest since 1983 and demonstrated a marked downward trend in fluoride contamination, which began in 1989 and continued through 1992. Except for a marginal exceedence at one of the forage sampling locations, there were no exceedences of established guidelines for fluoride in non-washed grass or silver maple foliage collected at any of the sites in 1991 or 1992. This contrasts sharply with surveys prior to 1989, which documented consistently elevated concentrations of fluoride in grass and tree foliage and associated foliar damage in the vicinity of the plant. There was no consistent relationship between soil fluoride concentration and foliar fluoride concentration. Slightly elevated concentrations of sulphur in silver maple foliage collected at a station close to the facility did indicate that the facility may be a marginal sulphur source, but the environmental signifigance is (likely) inconsequential. Uranium concentrations were below the detection limit in foliage and grass at all sites.

In general, the survey results indicate that impacts on the terrestrial environment in the vicinity

of the ICI facility have been significantly reduced as the result of action taken by the company to reduce fugitive fluoride emissions.

Figure 1: Sketch map of silver maple and soil sampling sites in the vicinity of ICI Lampton Works, Courtright.

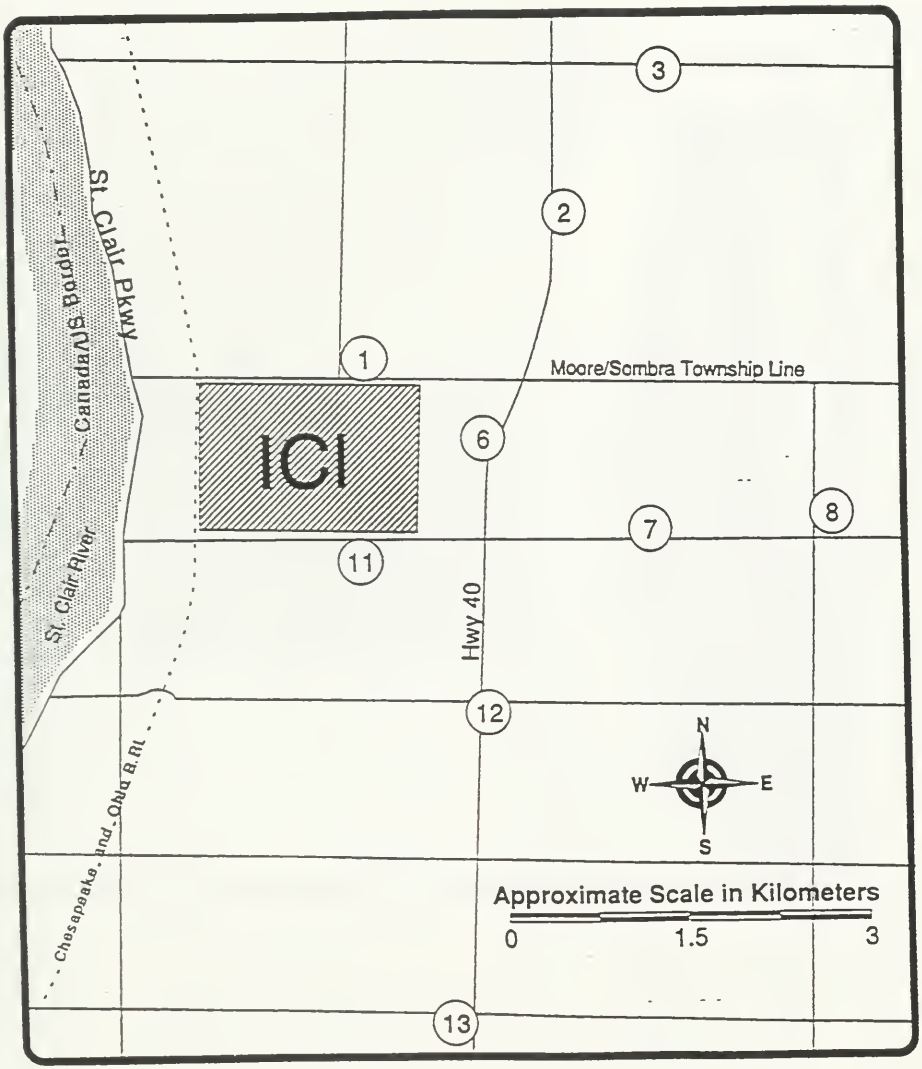

Figure 2: Sketch map of grass sampling sites in the vicinity of ICI Lampton Works, Courtright.

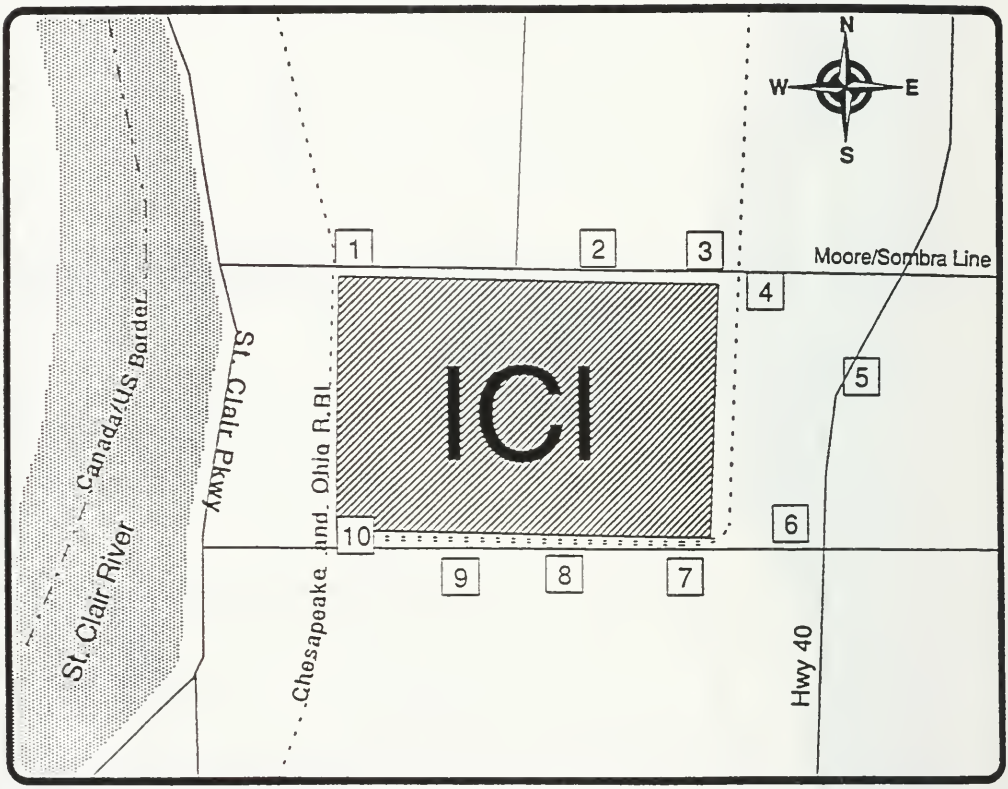

Table 1: Fluoride concentrations in washed and non-washed silver maple foliage collected in the vicinity of the ICI Lambton Works, Courtright, 1983-1992.

Site Number	Approx. Distance & Direction from CIL	Fluoride Concentration (ug/g - dry weight)[1]														
		1983		1984		1985		1986		1987		1989		1991		1992
		NW	W	NW	W	NW	W	NW	W	NW	W	NW	W	NW	W	NW
1	0.9 km NNE	337	293	668	550	464	448	435	440	670	630	160	90	15	14	7
2	3.0 km NNE	14	10	14	12	11	9	16	12	11	12	11	9	6	7	NS
3	4.5 km NNE	17	13	12	11	14	10	12	11	15	17	10	8	6	6	NS
6	1.4 km E	29	19	53	43	4	29	56	49	57	40	25	21	8	7	4
7	3.0 km E	19	12	15	13	9	8	16	9	12	9	13	10	6	6	4
8	4.5 km E	16	10	14	12	7	5	11	9	9	8	10	10	7	7	3
11	0.8 km SSE	84	55	101	96	160	97	165	140	330	315	55	44	9	8	4
12	2.6 km SSE	19	12	21	15	12	9	16	13	15	12	11	10	6	6	NS
13	5.0 km S	13	7	12	11	8	6	12	8	7	8	9	9	6	7	NS
Three Site Mean (1, 6 & 11)		150	122	274	230	222	191	219	210	352	328	80	52	11	10	NR
ULN		15	NG	15	NG	15	NG	15	NG	15	NG	15	NG	15	NG	15

1 Values represent the means of replicate samples.
NW - non-washed foliage samples
W - washed foliage samples
NS - no samples collected
NG - no guideline
NR - no result
ULN - Upper Limit of Normal Contaminant Guideline for fluoride in maple foliage collected from rural areas, see appendix.

Note: Values underlined exceed the ULN guideline for fluoride in maple foliage.

Table 2: Sulphur and uranium concentrations in washed and non-washed silver maple foliage collected in the vicinity of the ICI Lambton Works, Courtright, 1991.

Site Number	Approx. Distance & Direction from CIL	Sulphur Concentration (% - dry weight)		Uranium Concentration (ug/g - dry weight)	
		1991		1991	
		NW	W	NW	W
1	0.9 km NNE	0.30	0.32	DL	DL
2	3.0 km NNE	0.14	0.13	DL	DL
3	4.5 km NNE	0.14	0.13	DL	DL
6	1.4 km E	0.21	0.18	DL	DL
7	3.0 km E	0.15	0.16	DL	DL
8	4.5 km E	0.23	0.23	DL	DL
11	0.8 km SSE	0.17	0.14	DL	DL
12	2.6 km SSE	0.17	0.18	DL	DL
13	5.0 km S	0.17	0.16	DL	DL
Three Site Mean (1, 6 & 11)		0.23	0.21	NR	NR
ULN		0.40	NG	NG	NG

NW - non-washed foliage samples
W - washed foliage samples
NG - no guideline
NR - no results
ULN - Upper Limit of Normal Contaminant Guideline for sulphur in grass collected from rural areas, see appendix.
DL - at or below analytical detection limit (<0.05ug/g)
Note: Values represent the means of replicate samples.

Table 3: Fluoride concentrations grass collected in the vicinity of the ICI/CIL Lambton Works, Courtright, 1983-1992.

Site Number	Approx. Distance & Direction from CIL	Fluoride Concentration (ug/g - dry weight)							
		1983	1984	1985	1986	1987	1989	1991	1992
1	765 m WNW	11	21	8	6	14	5	2 T	1 T
2	250 m N	137	407	196	445	82	5	6	2 T
3	500 m ENE	23	48	76	80	89	9	4	1 T
4	850 m E	8	52	22	31	36	18	3	1 T
5	1300 m E	7	23	33	8	16	6	2 T	1 T
6	1000 m ESE	11	46	29	36	24	8	2 T	1 T
7	400 m ESE	24	151	127	105	36	56	7	3.8
8	200 m SSE	40	189	104	95	27	27	24	13.5
9	300 m SSW	8	85	63	88	23	12	7	2 T
10	700 m WSW	3	21	29	17	9	5	3	1 T
ULN		12							
AAQC[1] Flourides in Dry Forage		35 (avg. monthly [30 day] results for growing season) 60 (avg. of two consecutive months) 80 (avg. monthly results for any single month)							

ULN - Upper Limit of Normal Contaminant Guideline for fluoride in maple foliage collected from rural areas. Values underlined exceed the ULN guideline for fluoride in grass foliage, see appendix.

1 Ambient Air Quality Criteria contained in Regulation 296 under the Environmental Protection Act.

T A measurable trace concentration, interpret with caution.

Note: Values represent the means of replicate samples.

Table 4: Sulphur and uranium concentrations in grass collected in the vicinity of the ICI Lambton Works, Courtright, 1991.

Site Number	Approx. Distance & Direction from CIL	Sulphur Concentration (% - dry weight)	Uranium Concentration (ug/g - dry weight)
1	765 m WNW	0.2	DL
2	250 m N	0.3	DL
3	500 m ENE	0.2	DL
4	850 m E	0.1	DL
5	1300 m E	0.1	DL
6	1000 m ESE	0.1	DL
7	400 m ESE	0.2	DL
8	200 m SSE	0.2	DL
9	300 m SW	0.2	DL
10	700 m WSW	0.2	DL
ULN		0.5	NG

NG - no guideline
ULN - Upper Limit of Normal Contaminant Guideline for sulphur in grass foliage collected from rural areas, see appendix.
DL - at or below the detection limit (<0.05 ug/g)

Note: Values represent the means of replicate samples.

Table 5: Floride and radioisotope concentrations in surface soil collected in the vicinity of the ICI Lambton Works, Courtright, 1991.

Site Number	Approx. Distance & Direction from CIL	Fluoride	U-238	K-40	Ra-226
		ug/g	Bq/g dry wt.		
1	0.9 km NNE	180	< 0.05	0.85	0.05
2	3.0 km NNE	51	0.05	0.83	< 0.05
3	4.5 km NNE	61	< 0.05	0.72	< 0.05
6	1.4 km E	64	< 0.05	0.91	0.05
7	3.0 km E	46	< 0.05	0.66	< 0.05
8	4.5 km E	60	0.06	0.96	0.07
11	0.8 km SSE	170	< 0.05	0.88	0.06
12	2.6 km SSE	71	< 0.05	0.89	0.05
13	5.0 km S	78	0.06	0.95	0.07
Three Site Mean (1, 6 & 11)		138	< 0.05	0.88	0.05
ULN		NG	NG	NG	NG

ULN - Upper Limit of Normal Contaminant Guideline for sulphur in grass collected from rural areas, see appendix.
NG - no guideline
Bq/g - bequerels per gram
Note: Values represent the means of replicate samples.
U - Uranium K - Potassium Ra - Radium

Appendix

Derivation and Significance of the MOE Phytotoxicology "Upper Limits of Normal" Contaminant Guidelines.

The MOE Upper Limits of Normal (ULN) contaminant guidelines represent the expected maximum concentration in surface soil, foliage (trees and shrubs), grass, moss bags, and snow from areas in Ontario not exposed to the influence of a point source of pollution. Urban ULN guidelines are based on samples collected from developed urban centres, whereas rural ULN guidelines were developed from non-urbanized areas. Samples were collected by Phytotoxicology staff using standard sampling procedures (ref: Ontario Ministry of the Environment 1983, *Phytotoxicology Field Investigation Manual*). Chemical analyses were conducted by the MOE Laboratory Services Branch.

The ULN is the arithmetic mean, plus three standard deviations of the mean, of the suitable background data. This represents 99% of the sample population. This means that for every 100 samples which have not been exposed to a point source of pollution, 99 will fall within the ULN.

The ULNs do not represent maximum desirable or allowable limits. Rather, they are an indication that concentrations that exceed the ULN may be the result of contamination from a pollution source. Concentrations that exceed the ULNs are not necessarily toxic to plants, animals, or people. Concentrations that are below the ULNs are not known to be toxic.

ULNs are not available for all elements. This is because some elements have a very large range in the natural environment and the ULN, calculated as the mean plus three standard deviations, would be unrealistically high. Also, for some elements, insufficient background data is available to confidently calculate ULNs. The MOE Phytotoxicology ULNs are constantly being reviewed as the background environmental data base is expanded. This will result in more ULNs being established and may amend existing ULNs.